SOME CORRELATIONS OF THE EQUILIBRIUM THERMODYNAMICS OF THE ADSORPTION OF LIQUID MIXTURES AT SOLID-LIQUID INTERFACES

By

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In the thermodynamic treatment of the adsorption of liquid mixtures on a solid-liquid interface, the most important regularities determining the adsorption equilibria for the mixtures were analyzed primarily on the basis of the work of SCHAY and NAGY. A study was made of how the shapes of the excess isotherms are influenced by modification of the surface of the adsorbent and by systematic variation of the mosaic structure of the surface, and a new model isotherm equation relating to this was introduced. The specific free enthalpy of immersion wetting was calculated by integration of the excess isotherms, and the influence of the surface modification on the shapes of these functions was analyzed. It was demonstrated that the energy of interaction on the solid-liquid interface (for a given binary liquid mixture) depends to a decisive extent on the proportions of the hydrophilic and hydrophobic surface parts, that is on the surface heterogeneity.

Introduction

Liquid phase adsorption differs from gas adsorption in a number of respects. In the case of liquid adsorption the surface of the adsorbent can always be regarded as completely covered, and it is not the surface coverage which changes as a consequence of the surface forces (as in the case of gas adsorption), but the proportions of the liquid components in the interfacial phase. This means that the composition of the interfacial phase in general differs from that of the liquid phase in equilibrium with it.

The immersion method may be used for the quantitative determination of the adsorption of liquid mixtures; a known mass m of adsorbent is submerged in a quantity N° of the liquid mixture in question, in which the mole franctions of the components are x_i^0 initially and x_i after the adsorption equilibrium has been established. The specific excess adsorption of the liquid mixture (n_i^σ) can therefore be calculated by measurement of the change in concentration of the mixture, in accordance with the following relation:

$$n_i^\sigma = \frac{N^0}{m}(x_i^0 - x_i) = n_0 \Delta x_i \quad (i = 1, 2, \ldots) \tag{1}$$

The physical content of the adsorption excess isotherm for the mixture, $n_i^\sigma = f(x_i)$, is illustrated by the following mass balance for binary mixtures:

$$n^0 x_1^0 = n_1^s + (n^0 - n^s)x_1 \qquad (2)$$

The OSTWALD-de IZAGUIRRE equation is obtained free from all assumptions from the mass balance:

$$n^0(x_1^0 - x_1) = n_1^\sigma = n_1^s - n^s x_1 = n^s(x_1^s - x_1) \qquad (3)$$

where $n^s = n_1^s + n_2^s$ is the mass content of the interfacial phase (*e.g.* mmole/g), and $x_1^s = n_1^s/n^s$ is the mole fraction of the interfacial phase. According to eqn. (3), therefore, the excess isotherm arises from a combination of the "individual" isotherms $n_1^s = f(x_1)$ and $n_2^s = f(x_1)$. The excess isotherms found experimentally for the adsorption of binary liquid mixtures can be classified into five basic types [1, 2]. The magnitudes of the adsorption capacities can be determined from the excess isotherms by means of the analysis procedure of SCHAY and NAGY [1—3].

In the case of the purely physical adsorption of binary liquid mixtures which mix in all proportions, it is possible to describe the selective adsorption of the liquid mixtures on a solid adsorbent on the basis of the thermodynamics of ideal and regular mixtures [1]. SCHAY and NAGY primarily studied the roles of the differences between the properties of the components of the liquid mixture (differences between the sizes of the molecules, and the strengths of their interactions) in the development of the characters of the isotherms. It may be stated that a difference between the components of the mixture, as a factor affecting the adsorption equilibrium, appears as an activity coefficient in the thermodynamic treatment of a liquid mixture. Investigations were made to establish the extents to which the selective adsorption is influenced by the magnitudes of the activity coefficients, their ratio, and variations in them, *i.e.* to determine what types of excess isotherms are obtained for the various mixtures [4, 6].

The sum of the present work is to present the thermodynamics of the adsorption equilibria of liquid mixtures and to establish the correlations, and on this basis to study how modifications of the surface of the adsorbent and surface heterogeneities of the adsorbent can be characterized with the functions introduced. Further, we should like to demonstrate that changes in the composition of the interfacial phase and also the extent of selective liquid sorption are influenced significantly not only by the properties of the liquid phase, but by the mosaic structure of the surface of the adsorbent too.

Equilibrium constant for adsorption of a liquid mixture

It follows from the displacement nature of the adsorption of a liquid mixture that enrichment of one the components on the surface is possible only by the expulsion of the other component. Accordingly, the adsorption of binary mixtures can be described by the following exchange reaction scheme leading to equilibrium:

$$\beta(1) + (2)^s \rightleftharpoons \beta(1)^s + (2) \qquad (4)$$

where $\beta = a_{m,2}/a_{m,1}$ is the exchange constant characteristic of the exchange cross-sectional areas of components (2) and (1). The cross-sectional areas of the components of the mixture can be calculated from the molar volumes of the pure liquids at the temperature of the isotherm.

(The upper index s always refers to the interfacial phase.) The equilibrium constant of the exchange process is

$$K = \frac{a_2 (a_1^s)^\beta}{a_2^s (a_1)^\beta} \tag{5}$$

or, introducing the activity coefficients:

$$K = \frac{x_2 f_2}{x_2^s f_2^s} \left(\frac{x_1^s f_1^s}{x_1 f_1} \right)^\beta . \tag{6}$$

For ideal mixtures consisting of molecules of the same dimensions, it holds that $f_2/f_1 = 1$ and $\beta = 1$, and if it is further assumed that the interfacial phase too behaves ideally, *i.e.* $f_1^s/f_2^s = 1$, then eqn. (6) simplifies to the following form:

$$K_{\text{ideal}} = \frac{x_1^s x_2}{x_2^s x_1} = S \tag{7}$$

where S is the separation factor for the adsorption of the liquid mixture; this may be determined in the knowledge of the compositions of the interfacial phase and the homogeneous liquid phase. In the above special case, therefore, $K_{\text{ideal}} = S$, but in general the separation factor is not constant, but is a function of the composition x_1 [7].

If the cross-sectional areas of the components of the mixture are approximately the same ($\beta \approx 1$) and the activity coefficients of the interfacial phase compensate one another ($f_1^s/f_2^s \approx 1$), then eqn. (6) can be written in the following form:

$$x_1^s = \frac{x_1}{\frac{1}{K'} \frac{f_2}{f_1} (1 - x_1) + x_1} = \frac{a_1}{\frac{1}{K'} a_2 + a_1} . \tag{8}$$

According to this equation, the equilibrium diagram $x_1^s = f(x_1)$ describing the adsorption of the mixture is determined by the change in the activity of the homogeneous liquid phase and by the value of K'.

By taking into account eqn. (8) and $x_2^s = 1 - x_1^s$, we obtain for the separation factor S defined in eqn. (7):

$$S = K' \frac{f_1}{f_2} . \tag{9}$$

The activity coefficients are generally calculated from liquid-vapour equilibrium data, or in the case of regular mixtures on the basis of the HILDEBRAND equations [6].

Thermodynamics of a monomolecular adsorption layer

In the thermodynamic discussion of a monomolecular adsorption layer, our considerations are based on the generally used conception that the field of the adsorbent acts as an external field on the interfacial layer of the liquid [1]. In general, if some external force acts on the molecules of a homogeneous phase, its potential must be included in the more strictly taken chemical potential in order for us to be able to describe equilibrium distributions.

In accordance with the above train of thought, if an adsorbent is wetted by some pure liquid, and the potential of the field of the adsorbent referred to one mole of the surface layer is η_i, then the condition of equilibrium is

$$\mu_i^s + \eta_i = \mu_i^l \tag{10}$$

As regards the potentials η_i introduced in the above, it must be noted that they refer to the total surface of the adsorbent, and if this surface is energetically heterogeneous, then they are average values. Since the wetting is an exothermic process, η_i is negative, and thus $\mu_i^s > \mu_i$; this can be interpreted in that the liquid behaves as if it is under compression in the field of the adsorbent, and hence its chemical potential is in itself increased [1].

For the chemical potential we may write

$$\mu_i^s = \mu_i^0 + RT \ln a_i^s \quad \text{and} \quad \mu_i = \mu_i^0 + RT \ln a_i \tag{11}$$

It must be added that these equations refer to the same standard state; that is, a_i^s does not become unity if a pure liquid is in contact with the adsorbent [1].

For binary mixtures the equilibrium conditions given by eqn. (10) are

$$\mu_1^s + \eta_1 = \mu_1^l \quad \text{and} \quad \mu_2^s + \eta_2 = \mu_2^l. \tag{12}$$

According to the above:

$$\ln \frac{a_1^s a_2}{a_2^s a_1} = \frac{\eta_2 - \eta_1}{RT} \tag{13}$$

or if the activities are expressed as products of the activity coefficients and the mole fractions:

$$\ln \frac{x_1^s x_2}{x_2^s x_1} = \ln S = \ln \frac{f_1 f_2^s}{f_2 f_1^s} + \frac{\eta_2 - \eta_1}{RT}. \tag{14}$$

The above relation indicates that the extent of selective liquid adsorption is influenced not only by the activity coefficients, but also by the difference in the molar adsorption potentials.

If the condition $f_1^s / f_2^s \approx 1$ is accepted (calculations [5, 6] show this to be permitted), then from eqn. (14) we obtain a correlation formally identical to eqn. (8):

$$x_1^s = \frac{x_1}{\frac{f_2}{f_1}(1 - x_1) e^{-(\eta_2 - \eta_1)/RT} + x_1} \tag{15}$$

where K' in eqn. (8) is given by $K' = e^{(\eta_2 - \eta_1)/RT}$.

After the experimental determination of the excess isotherm for adsorption of the mixture according to eqn. (1), the equilibrium diagram $x_1^s = f(x_1)$ can be determined on the basis of eqn. (3), and the value of K' can be calculated from eqns. (8) and (15) in the knowledge of the activities. In most cases it may be stated that the value of K' varies with the equilibrium composition x_1. This means that the η_i values are not constant either, since it is much more probable that the potential energy of a molecule in the field of the adsorbent is also influenced by what liquid molecules are in its immediate environment, and thus η_i depends on the composition.

The effect of surface modification on selective liquid sorption

Our investigation on the adsorptions of mixtures on various natural silicate adsorbents (primarily montmorillonite and kaolinite) indicate that excess isotherms of type II are obtained in the case of a binary polar-apolar liquid mixture (*e.g.* alcohol-benzene); that is, the alcohols are preferentially adsorbed on the silicate surface. It can be seen in Fig. 1 that compared to the isotherm observed for the

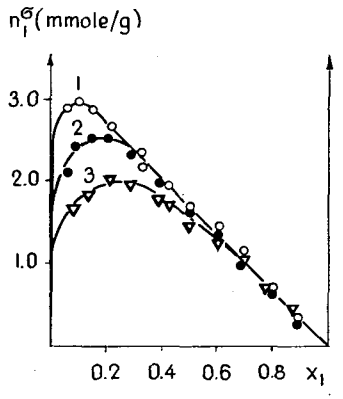

Fig. 1. Excess isotherms for adsorption of a liquid mixture on montmorillonites; 1. original, 2. sample treated with 1 : 1 water-isopropanol mixture, 3. sample treated with methanol. Mixture: methanol(1)-benzene(2)

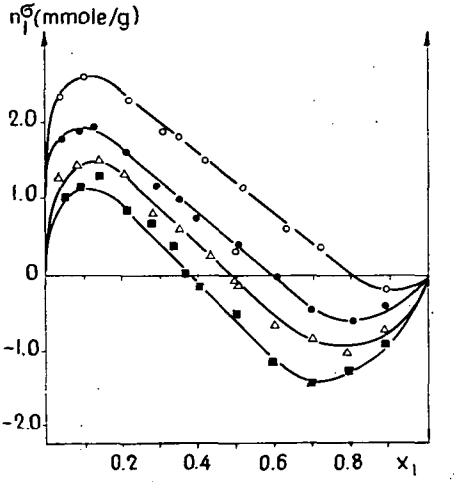

Fig. 2. Excess isotherms for adsorption of a liquid mixture on HDP-montmorillonites. Mixture: methanol(1)-benzene(2)

initially pure montmorillonite, the shapes of the isotherms are altered by pretreatment with alcohol; this may be explained by the chemisorption of the alcohols. This effect is essentially due to a slight surface modification. If the surface of the adsorbent is modified by some apolar compound (*e.g.* with hexadecylpyridinium cations by means of ion-exchange adsorption), the excess isotherms obtained for a polar-apolar mixture are of type IV; thus the apolar component is enriched in the interfacial

phase in a comparatively wide equilibrium concentration range [8—10] (Fig. 2). From analysis of the excess isotherms it can be stated that the adsorption capacity of the apolar component increases in proportion to the extent of the surface modification, and hence the components of the mixture are adsorbed *preferentially* on the surface parts of appropriate polarity. On the basis of concrete experimental data, this means that the magnitude of the surface part calculated from the adsorption capacity of the apolar component agrees well with the size of the modified surface part [11, 12].

Let us examine next how the value of K' can be correlated with the surface modification. Setting out from eqn. (6), let us assume that $\beta \approx 1$ and $f_1^s/f_2^s \approx 1$. For K' we then obtain:

$$K' = \frac{x_1^s x_2 f_2}{x_2^s x_1 f_1} = \frac{x_1^s a_2}{(1-x_1^s) a_1}. \tag{16}$$

Let us calculate the value of K' for the equilibrium composition x_1 where $a_2/a_1 = 1$. For the example of the methanol-benzene binary liquid mixture featuring in Table I, this composition is $x_1 = 0.68$. (For definitely regular mixtures the calculation must be carried out at a mole fraction $x_1 = 0.5$. (Since $x_1^s = n_1^s/n^s$ and $1 - x_1^s = n_2^s/n^s$, eqn. (16) can be written in the following form:

$$K'_{x_1=0.68} = \frac{x_1^s}{1-x_1^s} = \frac{n_1^s}{n_2^s} = K^*. \tag{17}$$

After WILLIAMS, the following equation may be written for a monomolecular layer completely covering the adsorbent:

$$n_1^s a_{m,1} + n_2^s a_{m,2} = a_{\text{equ.}}^s \tag{18}$$

where $a_{\text{equ.}}^s$ is the equivalent specific surface area. If eqn. (18) is divided by $a_{\text{equ.}}^s$:

$$\frac{n_1^s a_{m,1}}{a_{\text{equ.}}^s} = \theta_1 \quad \text{and} \quad \frac{n_2^s a_{m,2}}{a_{\text{equ.}}^s} = \theta_2 \tag{19}$$

i.e.

$$\theta_1 + \theta_2 = 1 \tag{20}$$

where θ_1 and θ_2 are the polar and apolar surface proportions, respectively. Hence, from eqns. (17) and (19), we obtain

$$K^* = \frac{\theta_1 \beta}{1-\theta_1} = \frac{(1-\theta_2)\beta}{\theta_2}. \tag{21}$$

If the value of K^* is substituted into eqn. (8), the equilibrium diagram can be calculated with the equation

$$x_1^s = \frac{x_1}{\frac{\theta_2}{(1-\theta_2)\beta}\frac{f_2}{f_1}(1-x_1) + x_1}. \tag{22}$$

The model isotherms calculated in accordance with the above equation and to be seen in Fig. 3 well illustrate the shapes of the functions that can be ascribed to the varius θ_2 values in the case of the binary methanol-benzene liquid mixtures.

If calculations are made with the apolar surface proportion $\theta_2 = a^s_{HDP}/a^s_{equ.}$ for hexadecylpyridinium-montmorillonites (HDP-montmorillonites) with surfaces modified to various extents, the model isotherms to be seen in Fig. 4 are obtained. (The characteristics of the adsorbents may be found in Table I).

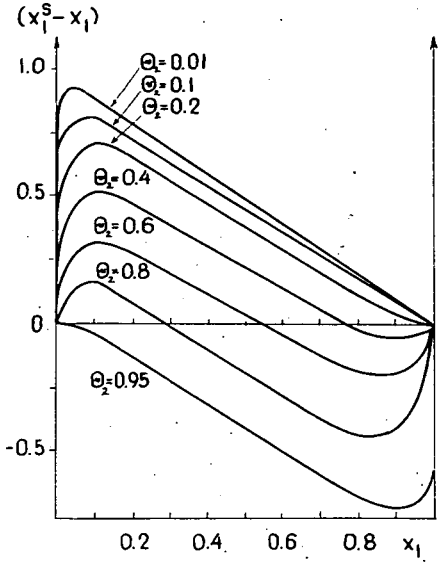

Fig. 3. Effect of surface modification on the shapes of the model isotherms on the basis of eqn. (22)

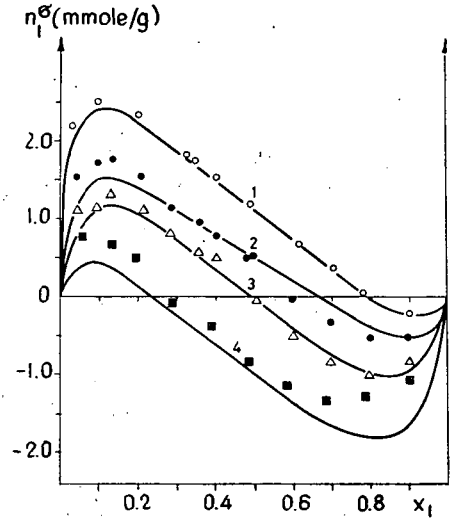

Fig. 4. Comparison of model excess isotherms and experimental data;
1. $\theta_2 = 0.326$, 2. $\theta_2 = 0.536$, 3. $\theta_2 = 0.635$,
4. $\theta_2 = 0.842$

Table I

Parameters characteristic of selective liquid sorption
Mixture: methanol(1)-benzene(2)

Adsorbent	HDP cation mequ./g	θ_2	$a^s_{equ.}$ (m^2/g)	$\varepsilon'_{2,0} - \varepsilon'_{1,0}$ (J/g)	$\Delta G^\sigma_{2,1}$ (mJ/m^2)	K (35) eqn.	K* (21) eqn.	x_1^a (24) eqn.	x_1^a exp.
montmorillonite	0.0	0.0	323	33.30	101.80	50.10	—	0.99	1.00
montm. (treated with methanol)	0.0	0.0	323	17.80	55.41	8.28	—	0.94	0.98
HDP-montm. I.	0.200	0.326	448	13.11	29.80	3.88	3.85	0.78	0.80
HDP-montm. II.	0.397	0.536	541	5.46	10.12	1.72	1.66	0.62	0.58
HDP-montm. III.	0.555	0.635	636	1.56	2.45	1.14	1.09	0.51	0.49
HDP-montm. IV.	0.683	0.678	733	0.59	0.80	1.06	0.99	0.47	0.43
HDP-montm. V.	0.812	0.773	764	−1.60	−2.10	0.88	0.59	0.36	0.37
HDP-montm. VI.	0.900	0.842	778	−2.85	−3.66	0.79	0.47	0.26	0.27

$$a_{m\,HDP} = 728\ m^2/mmol\ .\ \theta_2 = \frac{a^s_{HDP}}{a^s_{equ.}} \quad \beta = 1.8947$$

It can be seen that in the event of minor or moderate surface modifications the agreement with the experimental data is very good. The differences observed in the initial and final sections of the isotherm for the sample with $\theta_2=0.842$ can be explained by the appreciable desaggregation of the adsorbent (see the values of $a^s_{equ.}$ in Table I).

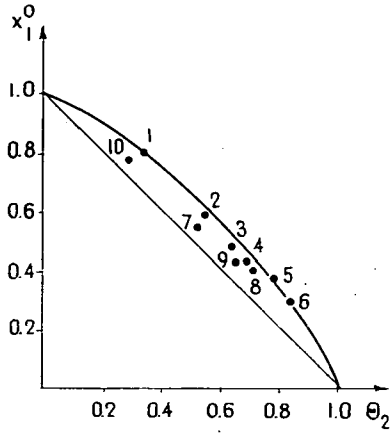

Fig. 5. Variation of the adsorption azeotrope composition with the surface modification according to eqn. (24)

The adsorption azeotrope composition (x^a_1) may also be correlated with the surface modification, for at the azeotrope composition the specific excess adsorption of the liquid mixture is

$$n^a_1 = n^s(x^s_1 - x_1) = 0, \quad \text{and so} \quad x^s_1 = x^a_1. \tag{23}$$

Hence, on the basis of eqns. (17) and (21), we may write

$$x^a_1 = \frac{K^*}{1+K^*} = \frac{\theta_1\beta}{\theta_2+\theta_1\beta}. \tag{24}$$

According to eqn. (24), the value of x^a_1 is determined to a first approximation by the magnitude of the polar-apolar surface ratio (*i.e.* by the mosaic structure of the surface), and also by β.

It can be seen in Fig. 5 and in Table I that the experimental x^a_1 values obtained for the adsorbent with its surface modified to various extents approximate very well to the function calculated with eqn. (24). Equation (24) provides a possibility for us to be able to characterize the mosaic structure of the surface of the adsorbent in the knowledge of the adsorption azeotrope composition.

Free enthalpy of immersion wetting

The thermodynamic laws regarding the interfacial interaction of a solid and a liquid can be expressed by the generalized equation of GIBBS—DUHEM type [1, 13]:

$$S^\sigma dT - V^\sigma dp + ZdF + \Sigma n^\sigma_i d\mu_i = 0. \tag{25}$$

In this equation, the notation σ means the corresponding excess of the extensive variables; the expression ZdF denotes the interfacial energy, written in general form, so that F is the corresponding intensity factor, and Z is the related extensive variable (*e.g.* it can be identified with the extent of the interface).

According to SCHAY [1], the generalized GIBBS—DUHEM equation can be written in the following concrete form for the adsorption of binary liquid mixtures on a solid surface:

$$S^{\sigma(2)}dT - V^{\sigma(2)}dp + m^a d\varepsilon' + n^{\sigma(2)}_1 d\mu_1 = 0 \tag{26}$$

where the index $\sigma(2)$ means the relative excess relating to component 2. In this equation the extensive variable Z is identified with m^a, the mass of the adsorbent, and the connected intensity factor will be denoted by ε'. An excess energy ε^a compared

to its compact state is characteristic of all extensively dispersed solid bodies (adsorbents) even in themselves, *i.e.* in vacuum, and the adsorption and wetting decrease this excess (exothermic adsorption and wetting heat). The notations

$$\varepsilon' = \varepsilon - \varepsilon^a \quad \text{and} \quad \varepsilon' < 0 \tag{27}$$

are introduced into eqn. (26) in such a sense. It should be noted that the corresponding correlations are usually written in general for ε instead of ε' in the relevant literature, or for the very problematical surface tension even in the case of a solid-liquid interface [14—16].

Under the customary conditions of experimental determination of liquid adsorption isotherms, *i.e.* at constant temperature and pressure, the form of the equation of the GIBBS adsorption isotherm valid for this case follows from eqn. (26):

$$-d\varepsilon' = \frac{n_1^{\sigma(2)}}{m^a} d\mu_1. \tag{28}$$

Since the following relations hold between the reduced and relative excesses [1]:

$$n_1^{\sigma(n)} = -n_2^{\sigma(n)} = x_2 n_1^{\sigma(2)} = -x_2 n_2^{\sigma(1)} \tag{29}$$

and since $d\mu_1 = RT\, d \ln a_1$, after the substitutions we obtain from eqn. (28):

$$-d\varepsilon' = RT \frac{n_1^{\sigma(n)}}{m^a x_2} d \ln a_1. \tag{30}$$

Integrating eqn. (30) over the total composition interval:

$$\varepsilon'(a_2 = 1) - \varepsilon'(a_1 = 1) = RT \int_{a_1=1}^{a_2=1} \frac{n_1^{\sigma(n)}}{x_2 a_1} da_1 \tag{31}$$

where $\varepsilon'(a_2=1) - \varepsilon'(a_1=1) = \varepsilon'_{2,0} - \varepsilon'_{1,0}$ is the difference in the excess energy changes relating to the interfaces between the solid and pure component 2 and 1, respectively. (The dimensions are, for example, joule/g or erg/g.) Integration of the excess isotherm is performed graphically, and it is beneficial to reckon with the specific excess adsorption of the liquid mixture, *i.e.* $m^a = 1$ g. Numerous references are to be found in the literature with regard to the application of eqn. (31) [17—19].

The variation of ε' as a function of the composition is illustrated in the following two Figures. The function to be seen in Fig. 6/A is obtained by integration of excess isotherms of types I, II and III; the value of the integral, $\varepsilon' - \varepsilon'_{1,0} = \Delta\varepsilon'$, is always positive. The function in Fig. 6/B arises from isotherms of types IV and V; in a certain range of composition, $\varepsilon' < \varepsilon'_{1,0}$, the value of the integral may also be negative [20—22].

By integration of our adsorption excess isotherms determined for liquid mixtures on montmorillonites and their organophilic derivatives [10, 11, 23], we calculated the variation of $\Delta\varepsilon'$ with the equilibrium composition in accordance with eqn. (31). It can be seen in Fig. 7 what functions are characteristic for the adsorption of a benzene-n-heptane mixture on montmorillonite and two organophilic montmorillonites (isotherm of type I).

Figure 8 demonstrates very illustratively how the course of the $\Delta\varepsilon'$ function is influenced by surface modification (organophilization) for a methanol-benzene mixture (isotherm of type IV). On the above basis it may be stated that adsorbents with different surface heterogeneities can be characterized in an exact way in a thermodynamic sense with the excess energy change calculated from integration of the excess isotherm.

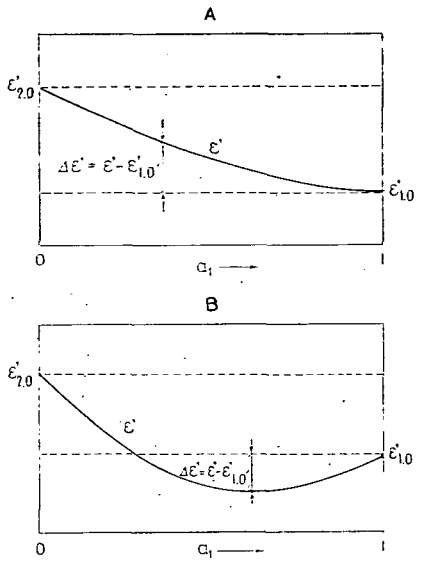

Fig. 6. Variation of ε' defined by eqn. (27) with the activity of the equilibrium homogeneous liquid phase

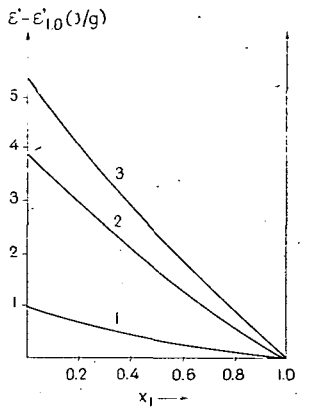

Fig. 7. Variation of $\Delta\varepsilon'$ with the equilibrium composition in the case of isotherms of type I; 1. montmorillonite, 2. $\theta_2 = 0.635$, 3. $\theta_2 = 0.842$

According to the thermodynamic laws of adsorption [1, 13], the excess free enthalpy can be given by the following equation:

$$G^\sigma = H^\sigma - TS^\sigma = FZ + \Sigma\mu_i n_i^\sigma. \tag{32}$$

In the case of the adsorption of binary liquid mixtures ($FZ = m^a\varepsilon'$):

$$G^{\sigma(2)} = m^a\varepsilon' + \Sigma\mu_1 n_1^{\sigma(2)}. \tag{33}$$

In the simplest case, when the adsorbent is immersed into a pure liquid, when adsorption does not occur in the sense of the GIBBS convention, since $n_1^{\sigma(2)} = 0$ and $m^a = 1$ g, eqn. (33) reduces to

$$G = \varepsilon' \tag{34}$$

where the ε' defined in eqn. (27) is equal to the specific free enthalpy of the immersion wetting, but ε' is not the same as the calorimetrically measured wetting enthalpy (immersion heat); the difference is given by eqn. (32). Hence, the value of $\varepsilon'_{2,0} - \varepsilon'_{1,0}$

obtained from integration of the excess isotherm is *the difference in the specific free enthalpies of immersion wetting in the pure components 1 and 2.* The notation $\Delta G^{\sigma}_{2,1}$ is used to indicate reference to unit surface area (see Table I).

The difference in the specific free enthalpies of immersion wetting in methanol(1) and in benzene (2) is depicted in Fig. 9 as a function of the surface modification.

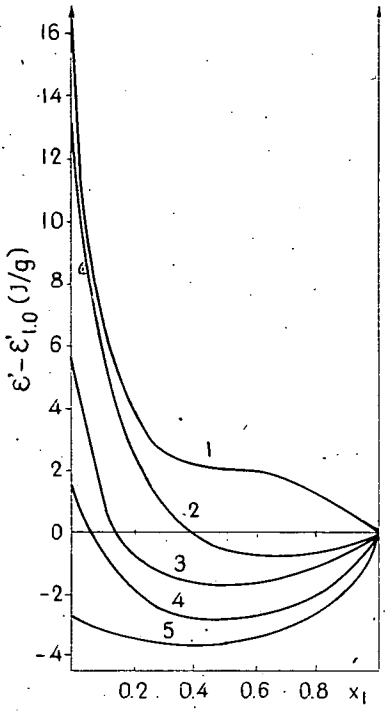

Fig. 8. Variation of $\Delta\varepsilon'$ with the equilibrium composition in the case of isotherms of type IV;
1. montmorillonite, 2. $\theta_2=0.326$, 3. $\theta_2=0.536$, 4. $\theta_2=0.678$, 5. $\theta_2=0.842$

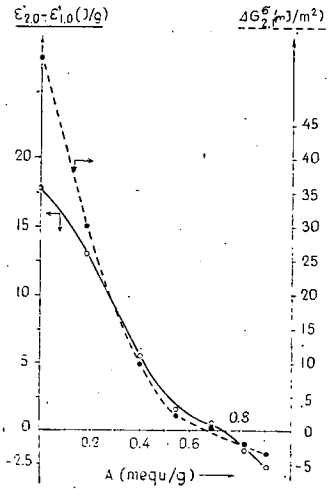

Fig. 9. Variation of the difference in specific free enthalpy of immersion wetting with the surface modification. A: HDP cation (mequiv./g)

The calculation show that the value of $\varepsilon'_{2,0}-\varepsilon'_{1,0}$, or $\Delta G^{\sigma}_{2,1}$, is considerable on the high-energy silicate surface; then, with increase of the apolar character of the surface, it decreases rapidly and changes in sign. The negative range (where $\varepsilon'_{2,0}<\varepsilon'_{1,0}$) is characteristic of organophilic montmorillonites of strongly hydrophobic character, with apolar surfaces.

Similar calculations were performed by PARFITT *et al.* [18] to characterize graphite surfaces with varius properties, with the essential difference that, instead of $\varepsilon'_{2,0}-\varepsilon'_{1,0}$, they calculate with the surface tension difference $\sigma^0_2-\sigma^0_1$, which is difficult to interpret in the case of a solid/liquid interface.

$\varepsilon'_{2,0}-\varepsilon'_{1,0}$ obtained by integration of the excess isotherms in accordance with eqn. (31) can be correlated with the equilibrium constant for adsorption of the liquid mixture [7, 16]:

$$\frac{\varepsilon'_{2,0}-\varepsilon'_{1,0}}{n^s RT} = \ln K \tag{35}$$

MYERS *et al.* [16, 17] state that the equilibrium constant K may be calculated in the following manner:

$$\frac{a^s_{\text{equ.}}(\sigma^0_2-\sigma^0_1)}{n^s RT} = \ln K. \tag{36}$$

According to eqn. (35), therefore, the constant K can be determined directly by integration of the excess isotherm over the total concentration interval. Strictly, however, the value of K is constant only if the adsorption capacity n^s too is constant; this is possible if the molecular dimensions of the components of the mixture are the same, *i.e.* if $\beta = a_{m,2}/a_{m,1} = 1$ [1, 7].

If the constant K determined in accordance with eqn. (35) is substituted in place of K' in eqn. (8) we may calculate the equilibrium diagram $x^s_1 = f(x_1)$ and, in the knowledge of n^s, the excess isotherm too. Our calculations confirmed that for the given system (by taking into consideration the activity coefficients) we do indeed obtain an isotherm approximating well to the experimental data; thus, our results can be regarded as thermodynamically consistent. In essence, the model isotherms to be seen in Fig. 3 confirm the applicability of the thermodynamic consistency test, with the difference that here calculations were made not with K, but with the K^* values defined in eqn. (21). On the other hand, it emerges from the data of Table I that the K values obtained by integration display an approximately good agreement with K^*, and therefore, on the basis of a comparison of eqns. (21) and (35), we may write:

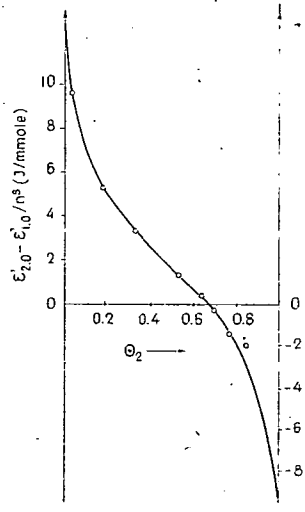

Fig. 10. Comparison of eqn. (37) with the experimental data

$$\varepsilon'_{2,0}-\varepsilon'_{1,0} \approx RTn^s \ln \frac{(1-\theta_2)\beta}{\theta_2}. \tag{37}$$

Thus, according to the above, the difference in specific free enthalpies of immersion wetting in liquids of different polarities is determined decisively by the apolar-polar surface ratio, and by the adsorption capacity. When the $(\varepsilon'_{2,0}-\varepsilon'_{1,0})/n^s$ values are calculated in accordance with eqn. (37) as a function of θ_2, the logarithmic function drawn as a continuous line in Fig. 10 is obtained. On the basis of eqn. (31), the integral values calculated with adsorbents of different organophilicities correspond to the course of the function.

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НЕКОТОРЫЕ ТЕРМОДИНАМИЧЕСКИЕ АСПЕКТЫ АДСОРБЦИИ ИЗ ЖИДКИХ СМЕСЕЙ НА ПОВЕРХНОСТИ ТВЕРДЫХ ТЕЛ

И. Декань и Л. Дь. Надь

Термодинамическое рассмотрение вопросов адсорбции из жидких смесей на границе раздела фаз жидкость-твердое тело проведено на основании изотерм адсорбции по работам Шай и Надя. Изучено влияние систематического изменения мозаичной структуры поверхности на вид кривых изотерм адсорбции и предложено новое уравнение изотермы адсорбции для таких случаев. Из уравнения изотермы рассчитана специфическая свободная энергия смачивания и проведен анализ влияния модификации поверхности на вид уравнений. Показано, что энергия взаимодействия на границе жидкость-твердое тело (для принятой бинарной смеси) зависит главным образом от соотношения гидрофильных и гидрофобных частей т. е. от мозаичности поверхности.